Plasma-based Defect Engineering of Graphene for Biosensing Applications

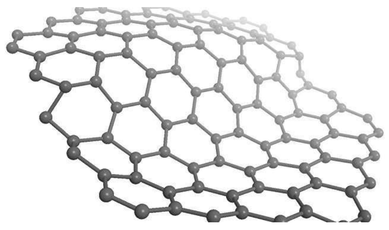
An Institute of NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE

Jordan Low Jun Yi, Koo Min Seo, Wong Yin Leng Angelina

NUS HIGH SCHOOL of Math & Science

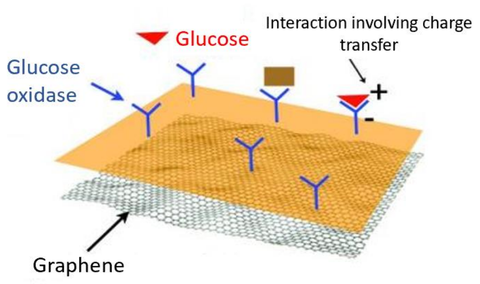
Background

- Diabetes mellitus is caused by insulin deficiency, resulting in elevated blood glucose levels
- Managed through monitoring of blood glucose levels with the aid of glucose biosensors.
- Graphene is a monolayer of carbon atoms arranged in a hexagonal lattice with large surface to volume ratio and high electrical conductivity.
- Used as an electrode surface in biosensors as its band structure is easily modified, and thus can amplify signals.



Research Aim

- In this project, plasma defects were engineered onto graphene surface to enhance immobilization of glucose oxidase (GOx) enzyme molecules for glucose-sensing applications.



- GOx anchored onto the graphene substrate via physical adsorption and catalyses the breakdown of glucose
- Low power RF plasma exposure introduces defects on the graphene surface
  → Increases surface adsorption of glucose oxidase enzyme
  → Leads to larger dynamic range of glucose sensing
- Quality of graphene ascertained using Raman spectroscopy
- Electrical properties of the graphene-based biosensor (GBB) monitored using an IV probe station.

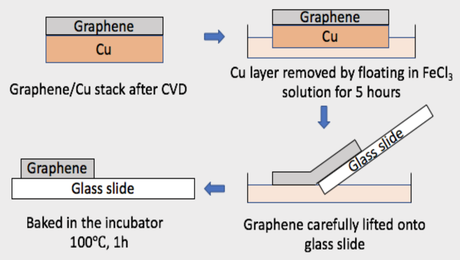
Materials and Methods

Graphene synthesis by Chemical Vapor Deposition (CVD)

- 10mm x 80mm copper (Cu) strip was placed in a horizontal quartz tube.
- Hydrogen gas was introduced, and the heat supply was switched on for the removal of contaminants.
- Methane gas was introduced for 1h to allow for the chemisorption of methane molecules to form the honeycomb pattern of graphene.

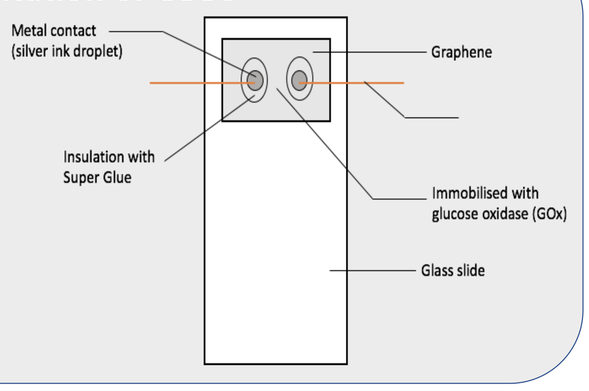
Graphene transfer

- The Cu layer was dissolved in $FeCl_3$
- Remaining graphene was transferred onto a glass slide and heated in an incubator at 100°C for 1h.



Implementation of GBBs

- 2 silver ink droplets with Cu wires attached used as metal contacts, which were insulated with water-insoluble superglue.
- Graphene surface immobilised with 1mg/dl GOx solution



Defect Engineering via RF plasma

- Each GBB placed within a horizontal quartz tube and hydrogen gas introduced at 26.5 SCCM.
- Capacitively coupled remote plasma switched on at 50W.
- GBBs exposed to 0, 5, 10, 15 and 20 min of plasma treatment.

▲ Experimental setup of defect engineering via RF plasma

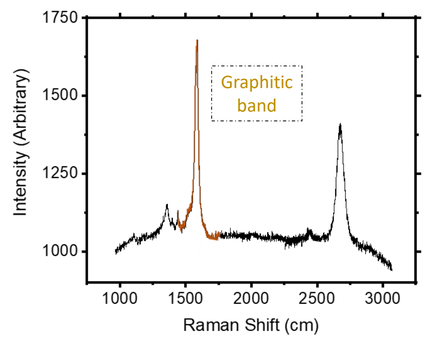
IV measurements

Resistance of biosensors measured using an IV probe station. Different concentrations of glucose were tested.

Results

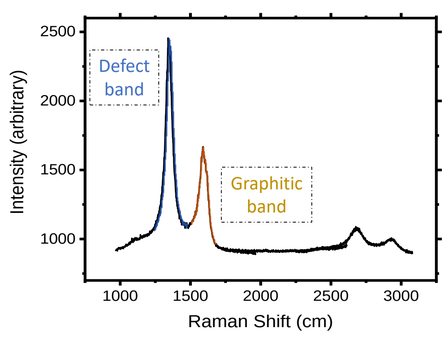
Raman Spectroscopy

Before plasma treatment:



- Raman Shift of the Graphitic band is 1587.94/cm
  → Graphene is a monolayer
- Defect band is weak
  → Graphene has little defects

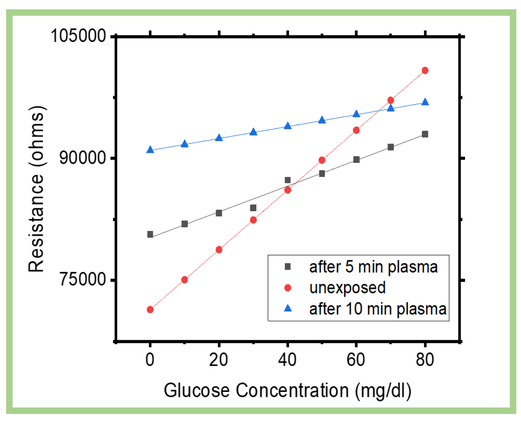
After plasma treatment:



- Raman Shift of the Graphitic band remains at 1587.94/cm
  → Graphene remained a monolayer
- Defect band is significantly larger
  → Defects had been introduced onto graphene

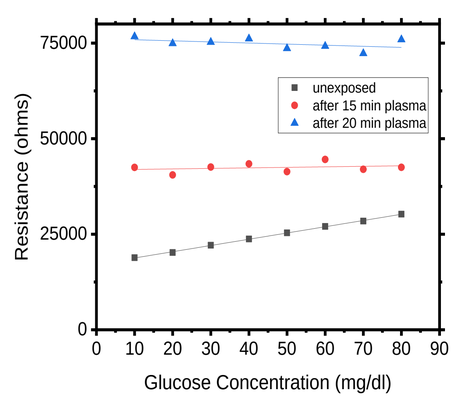
Raman shift of "G" band = $1581.6 + 11/(1 + n^{1.6})$

IV Characterisation



Exposure to plasma for 0, 5 and 10 min:

- Initial resistance increased for a longer exposure to plasma
- A longer exposure to plasma resulted in a gentler gradient



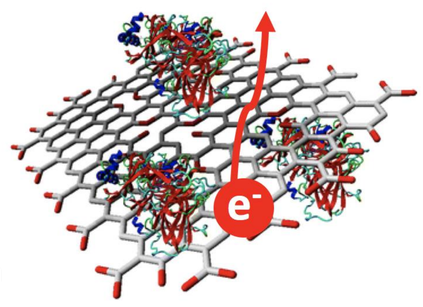
Exposure to plasma for 15 and 20 min:

- Increasing glucose concentration does not affect resistance
  - Plasma had resulted in defects to a degree that GOx is unable to bind effectively to graphene

Discussion

- Plasma causes defects to be introduced onto graphene
- Defects increase the surface area for adsorption of GOx onto graphene
- Each GOx molecule obstructs the movement of electrons, reducing electron mobility on the graphene surface

  ∴ Initial resistance increases with a longer duration of plasma treatment



$GOx\ (FADH_2) + O_2 \rightarrow GOx\ (FAD) + H_2O_2$
$Glucose + GOx\ (FAD^+) \rightarrow Glucolactone + GOx\ (FADH_2)$

- FAD is needed as a redox cofactor for GOx to function
- FAD present in glucose oxidase is first reduced to $FADH_2$
- $FADH_2$ reacts with oxygen, forming hydrogen peroxide and regenerating FAD
- FAD can continue to catalyse the oxidation of other glucose molecules

$Glucose + O_2 \rightarrow Glucolactone + H_2O_2$
$H_2O_2 \rightarrow H^+ + HO_2^-$

- H^+ and HO_2^- are electrophilic and causes the electron cloud to skew away from the graphene surface
- Lower concentration of mobile charge carriers on the surface of graphene causes an increase in resistance

  ∴ Resistance increases with glucose concentration

Conclusion

Graphene exposed to 5 & 10 minutes of plasma are best candidates as effective biosensors:

- 10 minutes of plasma:
  - Increase immobilization of GOx → achieve greater range of values
  - Greater reliance on specificity of GOx → compromises in accuracy.
- 5 minutes of plasma: Achieves a better accuracy while keeping a high range of values

Graphene exposed to 5 minutes of RF plasma in a depressurized chamber of 0.7 mbar of hydrogen gas with a flow rate of 26.5 SCCM is the most ideal biosensor.

Future Work

- Investigate other types of plasma to engineer defects on Graphene surface
- Explore more cost-effective ways to produce GBBs
- Study alternative electrode surfaces besides Graphene

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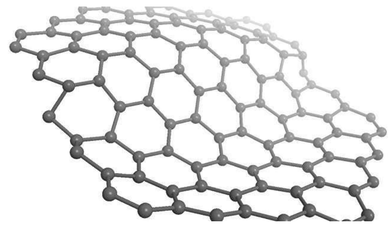

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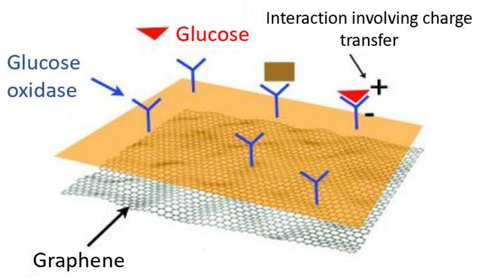

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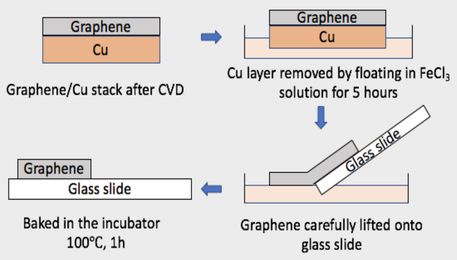

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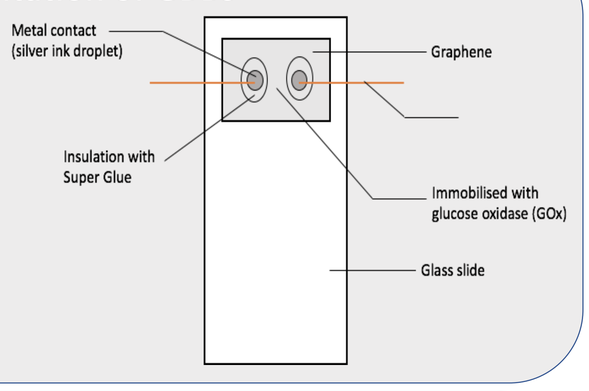

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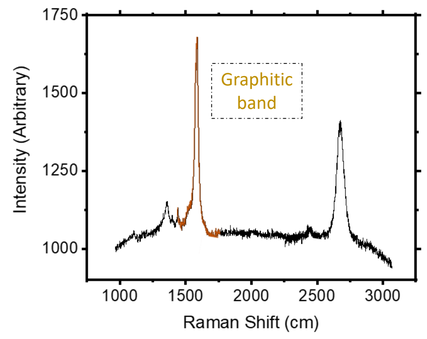

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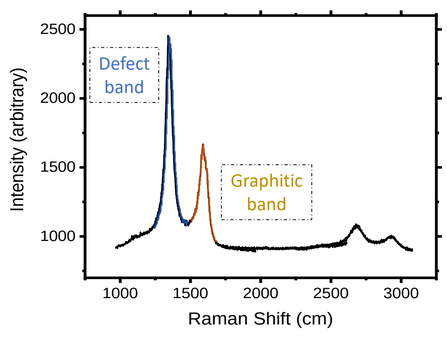

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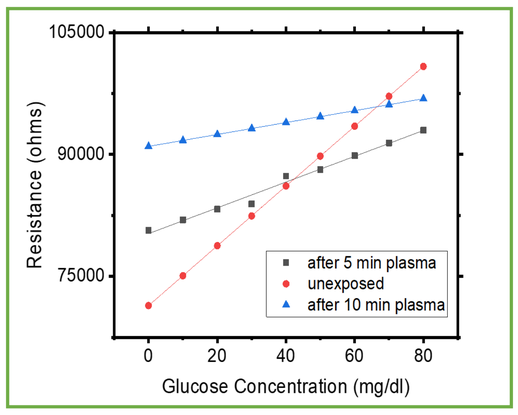

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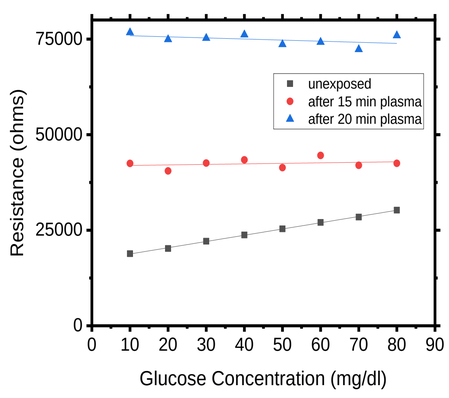

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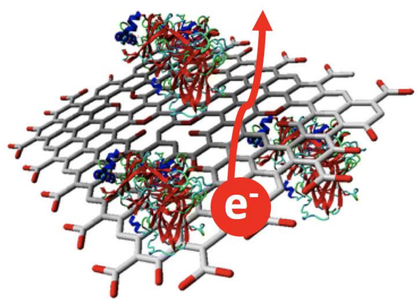

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